

# PATENT ABSTRACTS OF JAPAN

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## (54) PATINA COLOR EMITTING COMPOSITION LIQUID AND PATINA FORMING METHOD

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a patina color emitting composition liquid which acceleratively forms patina on copper or a base material formed by dispersing and solidifying the copper or a base material formed with a copper oxidized film and a patina forming method.

**SOLUTION:** The patina color emitting composition liquid prepared by compounding cupric chloride and sodium carbonate with an aqueous solution of one or ≥2 kinds selected from sodium chloride, aluminum chloride, zinc chloride and tin chloride and this liquid is applied onto the copper or the base material formed by dispersing and solidifying the copper or the base material formed with the copper oxidized film and is subjected to brushing, by which the composite type artificial patina of the basic cupric chloride and the basic copper carbonate is formed.

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**CLAIMS**

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**[Claim(s)]**

[Claim 1]Copper rust coloring presentation liquid which prepares a cupric chloride and sodium carbonate in one sort or two sorts or more of solution chosen from sodium chloride, an aluminium chloride, zinc chloride, and chloridation tin, and is characterized by things.

[Claim 2]A copper rust formation method forming compound-die artificial copper rust of the basic salt-ized second copper, and basic copper carbonate by applying and brushing the presentation liquid according to claim 1 on a substrate which carried out the distributed solidification of copper or the copper, or a substrate with which a copper acid-ized film was formed.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

[Field of the Invention] This invention relates to the copper rust coloring presentation liquid and the copper rust formation method which form copper rust precipitative on the substrate which carried out the distributed solidification of copper or the copper, or the substrate which the copper acid-ized film generated.

**[0002]**

[Description of the Prior Art] The method of making artificial copper rust form on a copper substrate and the presentation liquid (JP,4-193961,A) which generates copper oxychloride as artificial copper rust coloring liquid are proposed. The presentation of the copper rust coloring liquid which generates the basic salt-ized second copper of a proposal in this JP,4-193961,A, In order to oxidize treating solutions, such as an aluminium chloride, compulsorily, it is shown by adding oxidizers, such as manganese dioxide and anhydrous plumbic acid, that the basic salt-ized second copper is formed as a copper rust ingredient.

**[0003]**

[Problem(s) to be Solved by the Invention] However, the proposal of said JP,4-193961,A needed management of a part for strict humidity, and temperature in the copper rust coloring process of using the oxidation of manganese dioxide of the oxidizer added in coloring treatment liquid. Therefore, when artificial copper rust was formed on the base material surface of an outdoor structure, a large-sized heavy lift, etc., humidity control and temperature controlling become less enough, and there were many problems in forming copper rust. For example, since it is necessary to carry the equipment for humidity control and a temperature control when aimed at the roof of a height and a large-sized structure, trouble and danger are extremely accompanied by work. Then, in order that this invention persons may form copper rust on the base material surface of the existing Doya root, The oxidation, the strict humidity

control, and temperature controlling by an oxidizer of a conventional method are not needed, but it aims at proposing the copper rust coloring presentation liquid and the copper rust formation method which can generate artificial copper rust at an early stage on the base material surface of an outdoor structure, a large-sized heavy lift, etc. by oxygen in a part for natural humidity, and the atmosphere by an opened condition.

[0004]

[Means for Solving the Problem] This invention was proposed in view of the above, and relates to copper rust coloring presentation liquid which prepares a cupric chloride and sodium carbonate in one sort or two sorts or more of solution chosen from sodium chloride, an aluminium chloride, zinc chloride, and chloridation tin. This invention by also proposing a copper rust formation method which used said copper rust coloring presentation liquid, and applying and brushing said copper rust coloring presentation liquid on a substrate which carried out the distributed solidification of copper or the copper, or a substrate with which a copper acid-ized film was formed, In an opened condition, compound-die artificial copper rust of the basic salt-ized second copper, and basic copper carbonate came to acquire knowledge formed easily precipitative by \*\*\*\* operation (crystal deposit operation) of carbonate ion of sodium carbonate in copper rust coloring presentation liquid.

[0005]

[Embodiment of the Invention] A copper substrate points out a copper tabular material, a bar, a wire rod, and powder among the substrates with which this invention is applied, and copper with the substrate which carried out distributed solidification. Copper powder was mixed with resin and other inorganic substances, all the copper thermal-spraying raw materials which carried out thermal spraying of what has the coat containing copper powder which adhered to the surfaces, such as a resin board, with binders, such as resin, or the copper were pointed out, that in which the copper acid-ized film was formed also accepted in part the substrate with which the copper acid-ized film was formed to the entire surface, and it could be formed in it.

[0006] These substrates may be the raw material materials as construction materials, and may be roofing etc. of the already constructed outdoor construction (construction) thing. Although an outdoor structure in particular is not limited, it refers to all, such as a substrate used under the sea level of land or a sea structure, a marine vessel, a ship's bottom, etc. Namely, although artificial copper rust has the common use as construction roofing and the ornament and the artistic role are played on the other hand, The antibacterial activity of a copper rust ingredient can prevent adhesion of kelps, algae, and shellfish by being known for many years and forming artificial copper rust in the substrate used for the ship's bottom of a marine vessel and the structure of a harbor in the ocean.

[0007] In order to apply the copper rust coloring presentation liquid of said this invention on an above-mentioned substrate, a coating method like a publicly known throat can also be used,

and brush coating, roller coating in particular, etc. are not limited under a spray and a drop. The method of being immersed in the case of fine-arts mold goods etc. may be used. Since this invention does not need strict humidity control and temperature controlling like the conventional method, it is suitable for processing of an outdoor structure, but since a detrimental constituent is not generated, of course, indoor processing can be performed easily similarly. The shape of a base material surface cannot be limited, either, for example, artificial copper rust can be easily formed also on a rugged form substrate side.

[0008]Thus, this invention also receives an existing height like the Doya root and large-sized processing object (substrate) which are one of the outdoor structures, In the opened condition of natural environment, a special oxidizer is safely unnecessary and they are gas conditioning and a thing which can form the compound-die artificial copper rust of the basic salt-sized second copper, and basic copper carbonate in a short time comparatively by oxygen in a part for natural humidity, and the atmosphere without carrying out temperature control.

[0009]

[Function]An artificial copper rust generation operation of the copper rust coloring liquid of this invention is explained. In this invention, sodium chloride (NaCl), an aluminium chloride ( $AlCl_3$ ), . Are chosen out of zinc chloride ( $ZnCl_2$ ) and chloridation tin ( $SnCl_2$ ). The copper rust coloring presentation liquid which prepares a cupric chloride ( $CuCl_2$ ) and sodium carbonate ( $Na_2CO_3$ ) in one sort or two sorts or more of solution is applied on the substrate which carried out the distributed solidification of copper or the copper, or the substrate with which the copper acid-ized tunic was generated, and is brushed.

Therefore, copper (Cu) of a substrate is eluted and copper (Cu) concentration in the copper rust coloring presentation liquid gradually applied on the substrate becomes high, By the counteraction of sodium carbonate ( $Na_2CO_3$ ) in presentation liquid, and \*\*\*\* operation of a crystal deposit. The compound-die copper rust of basic copper carbonate ( $CuCO_3$  and  $3Cu(OH)_3$ ), and the basic salt-sized second copper ( $CuCl_2$  and  $3Cu(OH)_2$ ) is generated on a substrate.

[0010]

[Example][Example 1] 200 g of aluminium chlorides ( $AlCl_3 \cdot 6H_2O$ ) and 90 g of cupric chlorides ( $CuCl_2 \cdot 2H_2O$ ) were dissolved in the water 600g. The solution which dissolved in this solution in 160g of sodium carbonate crystals ( $Na_2CO_3 \cdot 10H_2O$ ) was added and prepared, and copper rust coloring presentation liquid was obtained. Membrane with high viscosity was generated by applying the obtained copper rust coloring presentation liquid on the Doya root which passed

after-construction three years in the atmosphere (humidity of 50 to 70%, temperature of 20-30 \*\*), and repeating brushing with the brush. The good artificial copper rust of adhesion was formed by neglecting this automatically. As a result of extracting a part of this artificial copper rust and conducting analysis by X-ray diffraction, it checked that it was the compound copper rust of the basic salt-sized second copper ( $\text{CuCl}_2$  and  $3\text{Cu}(\text{OH})_2$ ), and basic copper carbonate ( $\text{CuCO}_3$  and  $3\text{Cu}(\text{OH})_3$ ).

[0011][Example 2] 25 g of sodium chloride ( $\text{NaCl}$ ), 60 g of zinc chloride ( $\text{ZnCl}_2$ ), and 90 g of cupric chlorides ( $\text{CuCl}_2$  and  $2\text{H}_2\text{O}$ ) were dissolved in the water 200g. The liquid which dissolved 160 g of sodium carbonate crystals ( $\text{NaCO}_3 \cdot 10\text{H}_2\text{O}$ ) in this solution was added and prepared, and copper rust coloring presentation liquid was obtained. What mixed copper powder and was solidified with the synthetic resin on the cement plate was used as the substrate. The obtained copper rust coloring presentation liquid was applied on the above-mentioned substrate, and artificial copper rust was made to form according to said Example 1.

[0012][Example 3] What carried out surface roughening of the dry paint film which mixed copper powder with synthetic coating material on the metallic iron board was used as the substrate. The same copper rust coloring presentation liquid was applied on the above-mentioned substrate, and artificial copper rust was made to form according to said Example 1.

[0013][Example 4] What carried out thermal spraying of the copper and carried out surface roughening on the copper plate was used as the substrate. The same copper rust coloring presentation liquid was applied on the above-mentioned substrate, and artificial copper rust was made to form according to said Example 1.

[0014][Example 5] The artificial copper rust obtained in said Example 4 was hung to the structure of the harbor, it was immersed all over sea water, and the adhesion examination of marine algae and shellfish was done. As a result, even if immersed all over six-month sea water, there was no exfoliation of artificial copper rust, and there was no adhesion of marine algae and shellfish.

[0015]

[Effect of the Invention]As explained above, the copper rust coloring presentation liquid and the copper rust formation method of this invention, Since strict humidity control or temperature controlling are not needed like before, on the base material surface accompanied by the structure and the large-sized weight of indoor gas conditioning and not only the place by which temperature control was carried out but the outdoors, it can process in the atmosphere and artificial copper rust can be formed easily. Therefore, also when aimed at a height and a large-sized structure, for example, it can work easily and safely.

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[Translation done.]